

AD659956

Best Available Copy

NRL Report 6582

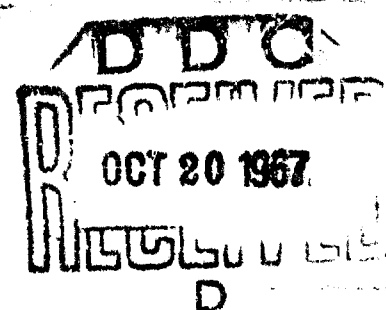
Halogenated Hydrocarbons

Part 2— Decomposition of Selected Chlorinated Hydrocarbons Over Hopcalite Catalyst

J. E. JOHNSON AND R. H. GAMMON

*Fuels Branch
Chemistry Division*

July 20, 1967



NAVAL RESEARCH LABORATORY
Washington, D.C.

Best Available Copy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
APPARATUS AND PROCEDURES	2
Apparatus	2
Analytical Techniques	2
Materials Used	3
Typical Experimental Procedure	3
RESULTS	4
Decomposition of 1,1,1-Trichloroethane (Methyl Chloroform)	4
Decomposition of 1,1-Dichloroethene (Vinylidene Chloride)	5
Decomposition of Trichloroethene (Trichloroethylene)	6
Decomposition of Tetrachloroethene (Tetrachloroethylene)	7
GENERAL DISCUSSION	8
Phosgene as a Potential Product	8
Decomposition of Methyl Chloroform	8
Decomposition of Vinylidene Chloride	9
Decomposition of Trichloroethylene	10
Decomposition of Tetrachloroethylene	11
SUMMARY AND CONCLUSIONS	11
RECOMMENDATION	12
ACKNOWLEDGMENTS	12
REFERENCES	12

ABSTRACT

A study was made of the decomposition of several chlorocarbons in air when exposed to Hopcalite catalyst in a laboratory reactor from 50° to 350°C. The chlorocarbons studied were methyl chloroform, vinylidene chloride, trichloroethylene, and tetrachloroethylene. At 300°C the percentage decomposition ranged from 70% for tetrachloroethylene to 100% for methyl chloroform. All yielded substantial amounts of hydrochloric acid as they decomposed. Yields of organic compounds during the decomposition of the chlorocarbons were quite small, except in the case of methyl chloroform, which yielded as much as 50% of vinylidene chloride.

PROBLEM STATUS

This is an interim report on the problem; work is continuing.

AUTHORIZATION

NRL Problem C08-30
Project SF 013-08-03-4092,4093,4094,4095

Manuscript submitted April 19, 1967.

HALOGENATED HYDROCARBONS

PART 2 - DECOMPOSITION OF SELECTED CHLORINATED HYDROCARBONS OVER HOPCALITE CATALYST

INTRODUCTION

Halogenated hydrocarbons have many industrial and commercial uses because of their excellent solvent power, high volatility, and reduced flammability. Owing to these and other useful properties many halogenated hydrocarbons are employed as solvents for adhesives, paint removers, cleaning fluids, and degreasing solutions, and as refrigerants and pressure can propellants.

Since halogenated hydrocarbons are used in the construction and operation of nuclear submarines, they are commonly found in the atmospheres of these vessels. One example is R-12, (CCl_2F_2), a common refrigerant used in the air conditioning systems of all nuclear submarines, which was detected in the earliest analyses of those submarine atmospheres (1). Other chlorofluorocarbons listed in publications to date as having been found in the atmospheres of nuclear submarines are R-114 (1-3) and R-11 (3). Some chlorocarbons, compounds containing chlorine but no fluorine, have been found also. An example is methyl chloroform (CH_3CCl_3) which has been used in large quantities as the solvent for contact adhesives in the application of insulation during construction of some nuclear submarines (4,5). Others include vinylidene chloride ($\text{CH}_2=\text{CCl}_2$)(4,5), trichloroethylene ($\text{CHCl}=\text{CCl}_2$)(3), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$)(3).

The principal disadvantages in the use of halogenated compounds are the corrosion resulting from the acidic vapors which are products of thermal decomposition and oxidation and the relatively high degree of toxicity possessed by some of these compounds and their decomposition products. An excellent example of an undesirable chlorinated solvent is carbon tetrachloride, CCl_4 . It is considered to be a toxic compound in its own right, and when heated under certain conditions it decomposes to give substantial yields of toxic phosgene and corrosive hydrochloric acid. Because of this the Navy does not allow its use aboard nuclear submarines or in most other applications. Some years ago a study was undertaken at NRL to find replacement solvents for carbon tetrachloride (6). It was concluded that the less toxic methyl chloroform would be preferable for use as a solvent, provided there is adequate ventilation.

Among the atmosphere control and purification equipment aboard nuclear submarines is the CO/H_2 burner, which employs a catalyst called Hopcalite to promote the combustion of carbon monoxide, hydrogen, and many organic compounds (7,8). This catalytic burner also tends to cause the decomposition of halogenated compounds which yield corrosive acidic products. For example, some corrosion which occurred in specific submarines (4) was traced to HCl resulting from the decomposition of methyl chloroform in the burner. Problems such as these have prompted limited laboratory studies of the decomposition of halogenated hydrocarbons in the past (7-9). However, the increasingly widespread commercial usage of halogenated compounds in many applications has stimulated more extensive examination of these compounds. Recently a detailed study was reported concerning the relative stabilities toward Hopcalite of a number of chlorofluorocarbons including the common refrigerants, R-11, R-12, and R-114 (10).

The present study is concerned with the products which result when the common solvents, methyl chloroform, trichloroethylene, and tetrachloroethylene, pass through the CO/H_2 burner in a stream of air. In addition, vinylidene chloride was included

because it also has been found in submarine atmospheres, most likely the decomposition product of methyl chloroform (5). It was this possible synthesis of other chlorinated compounds, in addition to the production of corrosive acids from the breakdown of these chlorinated solvents, which led to the more detailed study which is reported here of the interaction of these compounds with Hopcalite in the laboratory burner.

APPARATUS AND PROCEDURES

Apparatus

The laboratory apparatus used for these experiments was similar to that described earlier (7,8). A schematic diagram of the present unit is shown in Fig. 1. The insulated reactor unit was constructed from a 28-inch length of 1-1/8-inch-I.D. stainless steel tubing, which was mounted vertically to prevent voids in the catalyst space. The lower half of the reactor was filled with stainless steel turnings to serve as a preheater. This section, heated by Nichrome windings, controlled the temperature of the air entering the 5-inch deep catalyst bed. An air flow rate of 1 cfm, equal to a space velocity of $21,000 \text{ hr}^{-1}$, was used for most experiments except as noted. The same conditions of catalyst bed depth and space velocity are maintained in many CO/H_2 burners aboard nuclear submarines. Because of the low concentrations of contaminants involved, rubber and plastic materials were not used for construction of the equipment for handling the contaminated air stream. Only metal and glass were used downstream of the point of introduction of the contaminant.

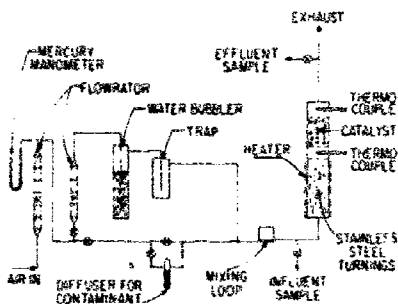


Fig. 1 - Schematic diagram of bench-scale reactor

The air mixtures containing desired concentrations of the chlorocarbons were prepared by passing a side stream of dry air through a diffuser containing the liquid contaminant as shown in Fig. 1. A constant temperature water bath was used to control the temperature of the diffuser. Unless otherwise stated the relative humidity of the air entering the reactor was maintained at 50 to 60% by control of the proportion of air which passed through the water saturator also shown in Fig. 1.

The identities of organic products found in the effluents during the decomposition reactions were confirmed by cross-checking retention times on several chromatographic columns. In the case of tetrachloroethylene found in the effluent from trichloroethylene additional confirmation was made by mass spectrometry.

Analytical Techniques

The analyses of the chlorinated hydrocarbons in the air stream were based on gas chromatography; a Beckman GC-2a unit with a hydrogen flame detector was used. The 8-foot, 1/4-inch-O.D. column was packed with 15% polyethyleneglycol 400 on Gas Chrom R. The relative retention times for the compounds of interest are given in Table 1. The samples of air were taken with an air-actuated Beckman sliding valve teamed with sampling loops of suitable size.

Analyses for hydrochloric acid in the burner effluent were made by using the NRL Acid Vapor Detector (11), a device for exposing a detector paper which is sensitive to strong acid gases. No quantitative significance is placed on the acid values found as

Table 1
Properties of Chlorinated Hydrocarbons

Common Name	L.U.C. Name	Structural Formula	Formula Weight	Normal Boiling Pt. ($^{\circ}$ C)	Relative G.C. Retention Time (min)*
Methyl Chloroform	1,1,1-Trichloroethane	$\text{CH}_3 = \text{CCl}_3$	133.42	74.0	5.6
Vinylidene Chloride	1,1-Dichloroethene	$\text{CH}_2 = \text{CCl}_2$	96.95	37.0	2.6
Trichloroethylene	Trichloroethene	$\text{CCl}_2 = \text{CHCl}$	131.40	87.2	10.0
Tetrachloroethylene	Tetrachloroethene	$\text{CCl}_2 = \text{CCl}_2$	165.85	121.2	13.0

*Based on 8-foot, 1/4-inch column packed with 15% polyethylene glycol 400 on Gas Chrom R at 70° C.

related to the actual amount of acid generated in the decomposition reactions studied because the Hopcalite catalyst is known to retain as halides significant amounts of the acids produced (7,8,10). However, the acid found in the effluent of the laboratory burner is significant as a relative indication of chlorocarbon decomposition, as well as in terms of the acid which might appear in the exhaust from the shipboard CO/H_2 burner under similar conditions. Gas detector tubes by Draeger Corp. and Mine Safety Appliances Co. were used to analyze for the potential presence of phosgene in the combustion effluents.

Materials Used

The catalyst used for all experiments was Hopcalite, a coprecipitate of manganese and copper oxides, manufactured by Mine Safety Appliances Co. and purchased through regular Navy supply channels. Further details concerning the physical and chemical analyses of the catalyst have been reported previously (7,8).

The lithium carbonate, which was mixed with Hopcalite for some experiments, was prepared by passing an air stream containing about 1% carbon dioxide through a bed of lithium hydroxide. The lithium hydroxide was obtained from Navy supply (12). The carbonate which was used contained less than 1% of free hydroxide.

The sources of the halogenated hydrocarbons were as follows: methyl chloroform from Phillips and Jacobs Co.; vinylidene chloride from Monomer-Polymer Laboratories of the Borden Company; trichloroethylene and tetrachloroethylene from Eastman Organic Chemicals Department. These compounds were used as received with the exception of trichloroethylene, which was distilled to remove traces of two lower-boiling contaminants including methyl chloroform. The vinylidene chloride used contained about 1.5% of trichloroethylene and < 1% of methyl chloroform. The overall purity of the vinylidene chloride was about 97%. The important properties of these chlorinated compounds are given in Table 1.

Typical Experimental Procedure

In a typical experiment the desired contaminant concentration was set up by making suitable adjustments in the operating conditions of the diffuser containing the liquid chlorocarbon. The air flow rate of the side stream of air, the diffuser temperature, and the throat diameter of the diffuser were the principal variables used to control the concentration of the contaminant in the air mixture entering the reactor. The temperature of the air stream leaving the preheater and entering the catalyst bed was set by adjusting the voltage on the autotransformer through which heat was supplied to the heater. Once the desired temperature was stabilized the contaminated air was allowed to pass through the reactor until successive gas chromatographic analyses of the influent and effluent air showed that equilibrium was attained. When sufficient data had been attained at a given temperature, the process was repeated at the next selected temperature.

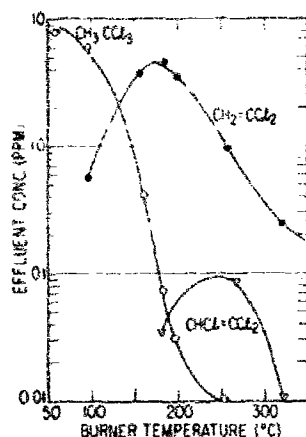


Fig. 2 - Decomposition of methyl chloroform, CH_3CCl_3 , in air over Hopcalite catalyst

To eliminate small variations in the contaminant concentration from the data curves such as in Fig. 2 the contaminant concentrations were normalized by reference of the influent contaminant peak to the air peak height for each sample. The data are plotted on semilog paper to show the concentrations of the chlorocarbons and products, which spanned more than two orders of magnitude in most cases.

RESULTS

Decomposition of 1,1,1-Trichloroethane (Methyl Chloroform)

(a) With Hopcalite Alone - Two runs were made in which methyl chloroform, $\text{CH}_3\text{-CCl}_3$, at 10 ppm in air was passed through the reactor at selected constant temperatures from 60° to 350°C. Each temperature was maintained constant until equilibrium was attained as shown by repeated analyses. The composite data from these two runs is plotted in Fig. 2.

Methyl chloroform was unstable under these conditions, showing some decomposition even at 60°C. At 100°C the effluent concentration of methyl chloroform had dropped to 6 ppm from an inlet concentration of 10 ppm. At less than 200°C, the methyl chloroform in the effluent was down to less than 1% of the entering concentration. This is interesting because it implies that essentially no methyl chloroform should survive the normal operating temperature of 600°F (315°C) prescribed for the CO/H_2 burners of nuclear submarines.

Two chlorinated hydrocarbons were detected as products in the decomposition of methyl chloroform. The major product and the first to appear was vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, which reached a maximum of 4.5 ppm at 185°C. Following this peak, the yield dropped until at 315°C only a few tenths of a ppm were found. It is deduced from these data that vinylidene chloride is considerably more stable than the parent compound, methyl chloroform. A much smaller yield of trichloroethylene, $\text{CCl}_3=\text{CHCl}$, was found in this decomposition reaction. The latter compound did not appear until a temperature was reached at which the methyl chloroform was essentially all gone, and it reached a maximum of less than 0.1 ppm. At 325°C no further evidence at trichloroethylene was found.

Under all conditions at which a significant proportion of the methyl chloroform decomposed in passing through the Hopcalite burner, substantial amounts of acid were found in the effluent from the burner. In the case of methyl chloroform with an entering

concentration of 10 ppm, a maximum of approximately 15 ppm of acid was found in the effluent. The reproducibility of the acid values was poor, undoubtedly due to the tendency of Hopcalite to retain variable amounts of acid depending on the previous use of the catalyst and on other conditions as observed previously (8-10).

(b) With Hopcalite Mixed With 10-Vol-% Lithium Carbonate - In current submarine practice the Hopcalite is mixed with 10-vol-% of lithium carbonate to assist in removing acid vapors from the effluent air. It was desirable to know what effect this admixture might have on the decomposition of methyl chloroform. Consequently two runs were made using the mixture in the reactor. The combined data are plotted in Fig. 3. The reproducibility of results at the same temperature is very good, as shown by the duplicate data points at several temperatures.

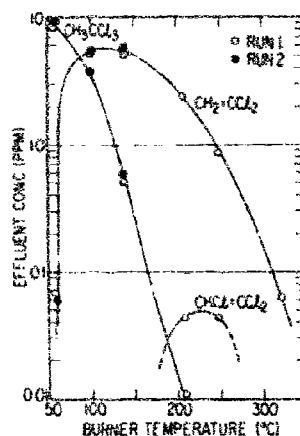


Fig. 3 - Decomposition of methyl chloroform, CH_3CCl_3 , in air over Hopcalite plus 10% v/v lithium carbonate

The decomposition curve for methyl chloroform in Fig. 3 is very similar to that in Fig. 2. The data indicate that the presence of lithium carbonate causes somewhat more decomposition at a given temperature. However, this difference is not very pronounced because of the extremely steep slope of the curves. Here again the major product was vinylidene chloride, which was formed at lower temperatures and also peaked earlier. The decomposition curves of vinylidene chloride in Figs. 2 and 3 are also very similar. Again, a small yield of trichloroethylene was found at about the same temperature as in Fig. 2, representing less than 1% of the original methyl chloroform.

Approximately 5 ppm of acid were found in the effluent from 250° to 320°C. These data showed that the lithium carbonate was not completely effective in preventing the issuance of acid gases in the exhaust from the burner. This fact is known from submarine experience also. Current submarine practice includes an additional lithium carbonate scrubber for the burner effluent gas downstream of the aftercooler. A detailed study of the effectiveness of various acid scrubbers has been issued recently (13).

Decomposition of 1,1-Dichloroethene (Vinylidene Chloride)

(a) With Hopcalite Alone - The data obtained for the decomposition of vinylidene chloride when passed through the reactor containing Hopcalite at 60° to 360°C are plotted in Fig. 4. The data were taken on two successive days, so the points on the graph are labeled Run 1 and Run 2. The excellent agreement between the overlapping points indicate again the precision of the gas chromatographic determinations as well as the good reproducibility of the experimental conditions.

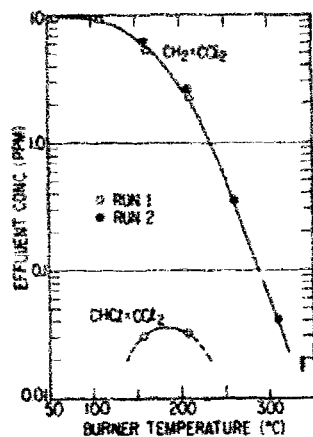


Fig. 4 - Decomposition of vinylidene chloride, $\text{CH}_2 = \text{CCl}_2$, in air over Hopcalite catalyst

The fact that about 25% of the vinylidene chloride was not decomposed at 210°C shows this compound to be more stable than methyl chloroform, which was decomposed at 200°C. However, at 310°C less than 1 ppm of the vinylidene chloride remained in the effluent. At 310°C and higher temperatures more than 10 ppm of acid were found in the effluent from a starting air mixture of 10 ppm of vinylidene chloride.

A very small yield, less than 0.5%, of trichloroethylene was found in the effluent at about 150° to 200°C. The values shown in Fig. 4 are corrected for the inlet impurity of trichloroethylene present in the original vinylidene chloride by using stability data from experiments starting with trichloroethylene. No other significant organic products were found in the effluent.

(b) With Hopcalite plus 10-Vol-% Lithium Carbonate - The decomposition of vinylidene chloride was studied in a system in which the reactor contained Hopcalite intermixed with 10-vol-% lithium carbonate. The data are given in Fig. 5. The decomposition curve is almost a duplicate of that in Fig. 4. There was no significant change with temperature in the decomposition rate of vinylidene chloride with lithium carbonate added to the Hopcalite. Again a trace, much less than 0.1% at maximum, of trichloroethylene was formed in the decomposition reaction. The acid content of the effluent gases was less with the carbonate than without. For example, at 300°C, with 10 ppm of vinylidene chloride in the influent air, the acid was 11 ppm without carbonate and 5 ppm with carbonate.

Decomposition of Trichloroethene (Trichloroethylene)

(a) With Hopcalite Alone - Data showing the decomposition of trichloroethylene when passed through the reactor containing Hopcalite from 60° to 355°C are given in Fig. 6. The data were taken on two successive days, so the points on the graph are labeled Run 1 and Run 2. Again the agreement between overlapping points is excellent.

Trichloroethylene was more stable than methyl chloroform or vinylidene chloride. About 60% of the trichloroethylene survived the burner at 200°C, whereas methyl chloroform was almost entirely decomposed, and only 25% of the vinylidene chloride survived. Approximately 25 ppm of acid were in the effluent air stream at 315°C from an initial charge of 10 ppm of trichloroethylene. Thirty ppm would be the theoretical maximum yield of hydrochloric acid.

Tetrachloroethylene was found in the effluent with a maximum yield of a little more than 1% at 265°C. A trace of dichloroacetylene was found also.

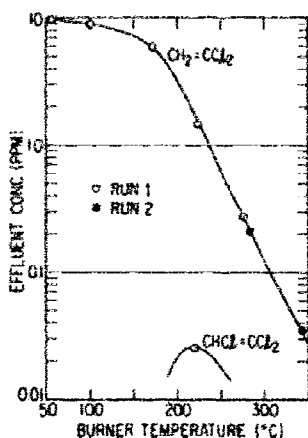


Fig. 5 - Decomposition of vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, in air over Hopcalite plus 10% v/v lithium carbonate

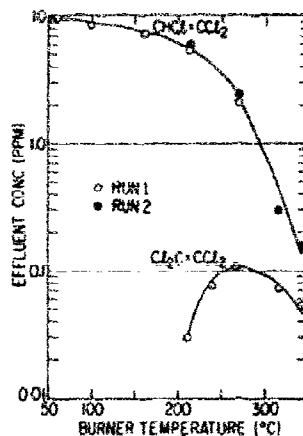


Fig. 6 - Decomposition of trichloroethylene, $\text{CHCl}=\text{CCl}_2$, in air over Hopcalite catalyst

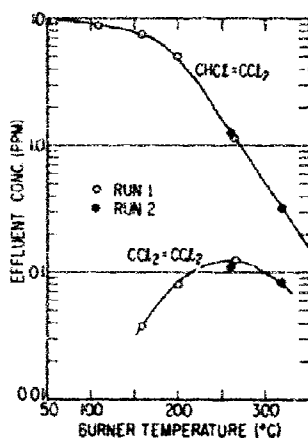


Fig. 7 - Decomposition of trichloroethylene, $\text{CHCl}=\text{CCl}_2$, in air over Hopcalite plus 10% v/v lithium carbonate

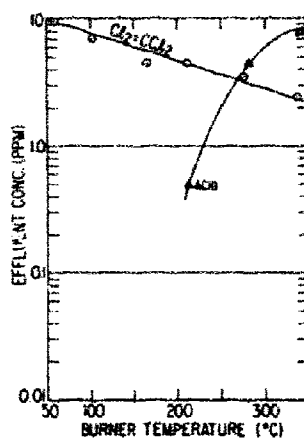


Fig. 8 - Decomposition of tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$, in air over Hopcalite catalyst

(b) With Hopcalite Plus 10-Vol-% Lithium Carbonate - The decomposition of trichloroethylene over Hopcalite with 10-vol-% admixture of lithium carbonate is shown in Fig. 7. There appears to be no significant effect due to the added lithium carbonate, and the decomposition curve is almost the same as in Fig. 6, without lithium carbonate. Again a little more than 1% yield of tetrachloroethylene at the maximum was found. At 315°C, 8 ppm of acid was found compared to 25 ppm without lithium carbonate.

Decomposition of Tetrachloroethene (Tetrachloroethylene)

With Hopcalite Alone - Tetrachloroethylene was the most stable of the chlorocarbons studied over Hopcalite, as shown by the data in Fig. 8. Although at 200°C about 50% of

this compound decomposed, about the same percentage decomposition as for trichloroethylene at 200°C, tetrachloroethylene was more stable at higher temperatures. For example, at 300°C about 70% decomposition of the tetrachloroethylene occurred, according to the curve in Fig. 8, whereas at the same temperatures 95% of the trichloroethylene had decomposed. The difference in the two curves is the sharp change in slope of the curve at about 200°C for trichloroethylene, which is absent in the case of tetrachloroethylene. A significant amount of acid was found, roughly one mole of acid per mole of tetrachloroethylene destroyed, as shown by the data for acid content given in Fig. 8. No peaks were observed in the chromatograms which might be due to organic products.

GENERAL DISCUSSION

Several general observations emerge from the data presented in this report. The order of the compounds in regard to increasing stability toward Hopcalite in the temperature range of 250°C to 350°C was found to be $\text{CH}_3\text{-CCl}_3 < \text{CH}_2=\text{CCl}_2 < \text{CHCl=CCl}_2 < \text{CCl}_2=\text{CCl}_2$. At lower temperatures the relative stabilities were interrelated in a more complex manner.

Upon decomposition, all four of these compounds yielded substantial amounts of hydrochloric acid. Methyl chloroform yielded as much as 50% vinylidene chloride and was the only chlorocarbon studied from which a significant yield of an organic product was obtained. Addition of lithium carbonate to the Hopcalite did not cause a significant change in the decomposition rates of the chlorocarbons.

Each chlorocarbon will be discussed in detail in the following sections, as will the significance of a potential product, phosgene.

Phosgene as a Potential Product

No evidence was found for the presence of phosgene in the effluent during the decomposition of any of the four chlorocarbons studied. In several instances, concentrations of chlorocarbons in the influent were increased to 50 ppm to facilitate detection of phosgene. It is estimated that the detector tube method used would permit the detection of phosgene at about 1% of the entering chlorocarbon concentration. The absence of phosgene in the decomposition products is obviously important to the habitability of submarine atmospheres or any closed atmosphere system.

Crummet and Stenger (14) published data on the formation of phosgene during the decomposition of chlorinated hydrocarbons in air when passed over iron at temperatures up to 700°F (371°C). Carbon tetrachloride yielded 275 mg phosgene per gram of solvent, whereas with methyl chloroform the yield was only 0.8, with trichloroethylene 2.3, and with tetrachloroethylene 0.1 mg. In other words, except for carbon tetrachloride, these compounds all yielded less than about 0.2% phosgene. Stefanescu (15) also found a trace of phosgene during the decomposition of methyl chloroform in air over iron, as well as over copper, zinc, aluminum, and bronze at temperatures from 150° to 350°C and higher. High yields of phosgene were obtained from carbon tetrachloride over iron at 240° to 340°C. The available literature generally agrees that the decomposition of methyl chloroform, trichloroethylene, and tetrachloroethylene on various surfaces yield little or no phosgene. The present work extends this agreement to include Hopcalite catalyst.

Decomposition of Methyl Chloroform

Barton and Onyon (16) found that methyl chloroform (1,1,1-trichloroethane) when pyrolyzed at 360° to 435°C in the absence of other gases decomposed to give vinylidene chloride and HCl. They concluded that the decomposition proceeded by both a unimolecular

and a radical chain mechanism occurring simultaneously. The chain process was believed to involve chlorine atoms. The chain reaction, however, was found to be inhibited readily by olefins, including the product vinylidene chloride, and by surfaces. In any case, the reaction products can be represented by the simple equation



Crummett and Stenger (14) were apparently the first to publish data concerning the stability of methyl chloroform in air in contact with heated metals. However, they analyzed only for the specific potential products, phosgene and HCl. They found that the metals studied fall into two groups in terms of effectiveness toward the decomposition of methyl chloroform vapor in air to yield HCl. Copper, cast iron, and steel caused a high yield of HCl at 282°C. Zinc, brass, and aluminum were relatively ineffective.

The present study of the decomposition of methyl chloroform over Hopcalite is in general agreement with the literature cited. It was found that Hopcalite does decompose methyl chloroform to yield primarily vinylidene chloride and HCl.

The presence of small amounts of trichloroethylene in the effluent from the decomposition of methyl chloroform can be traced to the possible attack of Cl atoms on the product vinylidene chloride to yield a radical -CH=CCl_2 which can decompose further or add a Cl atom to form trichloroethylene. There is no general agreement in the literature upon a mechanism beyond the initial attack of the chlorine atom or other radical to remove a hydrogen atom. Although no direct comparison is possible, it seems clear that Hopcalite enhances the decomposition rate at a given temperature in comparison with metals and quartz (14,15).

Decomposition of Vinylidene Chloride

Barton and Onyon (16) found that vinylidene chloride showed no decomposition at 412°C after 15 minutes in a static system in the absence of air. This is in contrast with the substantial decomposition they found for methyl chloroform under the same conditions. More recently Molera and Ariza (17) obtained measurable pyrolysis of vinylidene chloride at 494° to 555°C and calculated an activation energy of 35.3 kcal/mole for its decomposition.

The present work also showed that vinylidene chloride is considerably more stable than methyl chloroform over Hopcalite. At 160°C, where methyl chloroform was essentially all decomposed, vinylidene chloride had decomposed to the extent of 35%. Here again the decomposition over Hopcalite was much greater than had been reported in glass (17). If the decomposition followed the simple mechanism of a loss of one mole of HCl per molecule, the following would be expected:



The data given in Fig. 4 show that the decomposition of vinylidene chloride over Hopcalite yields large amounts of HCl. However, no definite evidence was found for the presence of chloroacetylene, CH=CCl , in the burner exhaust. In fact, no product peaks which represented as much as 1% of the original compound appeared in the chromatograms of the effluent samples. This result is not unexpected in view of the low stability of chloroacetylene in air (18).

The superior stability of vinylidene chloride relative to methyl chloroform found in these studies is consistent with data obtained for samples of air from inlet and exhaust of a shipboard burner (4,5). These samples were analyzed in the laboratory with results as given in Table 2. These data show that methyl chloroform is almost completely

destroyed in the shipboard burner by Hopcalite at 800°F (315°C) with vinylidene chloride as a major product. Vinylidene chloride is stable enough to survive the burner to some extent, showing an actual increase as the methyl chloroform disappears. The data also show that the concentrations of both chlorinated compounds dropped as the submergence continued from 15 hours to 20 hours, showing that vinylidene chloride, the decomposition product of methyl chloroform, is in turn eventually destroyed by the burner.

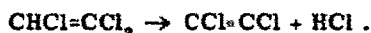
Table 2
Chlorinated Compounds in Ship's Atmosphere*

Sample No.	CO/H ₂ Burner Location	Submergence (hours)	Methyl Chloroform (ppm)	Vinylidene Chloride (ppm)
1	Inlet	15	6.1	1.6
2	Exhaust	15	0.1	2.1
3	Inlet	20	2.2	0.5
4	Exhaust	20	0.04	1.1

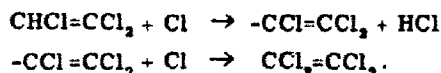
*Samples of atmosphere taken aboard an FBM submarine and analyzed in the Laboratory. Data are taken from Ref. 4.

Decomposition of Trichloroethylene

Earlier works, e.g., Sjöberg (19), showed that trichloroethylene, $\text{CHCl}=\text{CCl}_2$, in contact with metals heated from 100° to 500°C (19) decomposed in air to yield HCl and very little phosgene. Also it has been reported by many workers (20) that trichloroethylene in contact with hot alkali yields dichloroacetylene, as follows:



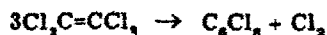
The data in Figs. 6 and 7 show that trichloroethylene is fairly stable over Hopcalite up to about 200°C with an increasing rate of decomposition beyond this point. It was estimated that as much as two moles of HCl were obtained per mole of trichloroethylene. However, only trace amounts of dichloroacetylene were found in the effluent. A small yield, about 1% maximum, of tetrachloroethylene was found. The appearance of this fully chlorinated ethylene tends to support the theory of Barton and Onyon (16) for formation and participation of chlorine atoms in the decomposition reactions of chlorinated hydrocarbons. Here again attack by Cl atom would likely be



There is no general agreement concerning the attachment of a Cl atom to the radical. However, the products found in the thermal decomposition of many other chlorine compounds seem to indicate an abundance of chlorine atoms for attachment or rearrangement reactions. Nicodemus (21) reported that tetrachloroethylene was found in the products collected from the decomposition of trichloroethylene in a quartz tube. He also suggested that dichloroethylene was formed with subsequent decomposition and polymerization. Erdmann (22) found that trichloroethylene oxidizes in air at relatively low temperatures to yield phosgene and HCl . At higher temperatures CO is also formed, which may indicate an intermediate stage of dichloroacetylene which is known to react with O_2 to yield CO and phosgene. The formation of dichloroacetylene from trichloroethylene under various conditions and subsequent decomposition is a complex subject which will be dealt with in a later report.

Decomposition of Tetrachloroethylene

The decomposition of tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$, which contains no hydrogen atoms, would be expected to differ from the dehydrochlorination type of monomolecular decomposition which apparently is the most likely occurrence over Hopcalite for organic compounds containing both hydrogen and chlorine atoms. Sjöberg (19) found very little phosgene in decomposition of tetrachloroethylene in air over iron and other metals. It is of interest also that tetrachloroethylene vapor was found by Krynitsky and Carhart (23) to be quite thermostable in Pyrex vessels in the absence of other gases, as no pyrolysis products were found on heating to 500°C . Molera and Ariza (17) studied the gas phase pyrolysis of $\text{CCl}_2=\text{CCl}_2$ in absence of air also and found measurable decomposition to occur between 720° and 800°C . A solid product, which proved to be hexachlorobenzene, was found in addition to small amounts of other solids including carbon. On this basis they suggested the following two decomposition reactions:



The present work with Hopcalite is summarized in Fig. 8. It is evident that tetrachloroethylene is the most stable of the four compounds studied. No significant additional peaks were found in the burner effluents, although conditions for analysis would not have detected hexachlorobenzene if it had been a product. The fairly good yields of acid indicate that much of the chlorine from the tetrachloroethylene was exhausted as hydrochloric acid, probably from interaction of chlorine atoms or molecules with water vapor in the air stream.

SUMMARY AND CONCLUSIONS

Four chlorinated hydrocarbons (methyl chloroform, vinylidene chloride, trichloroethylene, and tetrachloroethylene) were studied in a laboratory reactor with regard to decomposition in an air stream over Hopcalite catalyst from 50° to 350°C . The results can be summarized as follows:

All four of the chlorocarbons studied decomposed to a substantial degree under these conditions at 300° to 335°C , the approximate current operating range of the CO/H_2 burners aboard nuclear submarines. The percentage decomposition at 300°C ranged from 100% for methyl chloroform to 70% for tetrachloroethylene, the most stable compound studied.

All four compounds yielded significantly large amounts of hydrochloric acid as they decomposed. At the higher temperatures the yield was one mole or more of acid per mole of chlorocarbon destroyed.

The rates of decomposition of the chlorocarbons and the yields of organic products were not appreciably altered by the admixture of 10% lithium carbonate with the Hopcalite. The acid content in the effluent air was reduced, but a substantial percentage came through nevertheless.

Only in the case of the decomposition of methyl chloroform was a substantial yield of an organic product produced. Yields of vinylidene chloride as high as 50% were obtained at temperatures of 150° to 250°C . A maximum yield of about 1% of trichloroethylene occurred also.

A small yield of trichloroethylene, maximum of about 0.3% near 200°C, was obtained when vinylidene chloride decomposed. Trichloroethylene yielded about 1% of tetrachloroethylene at about 250°C. Much smaller yields of dichloroacetylene were observed also. No organic products were found when tetrachloroethylene decomposed over Hopcalite.

No evidence was found for the presence of phosgene during the decomposition of these four chlorocarbons.

RECOMMENDATION

In view of the catalytic decomposition of the chlorinated hydrocarbons studied to give large yields of hydrochloric acid and, in some cases organic chlorocarbons, it is recommended that special efforts be made to avoid the use of halogenated hydrocarbons in nuclear submarines or other closed environments, particularly where devices for catalytic oxidation are used.

ACKNOWLEDGMENTS

We are indebted to Dr. Barry Bronfin, formerly of the Fuels Branch, Code 6180, and now with Avco Corp., and Mr. Foster J. Woods of the Fuels Branch, for aid in planning some of the equipment and procedures, and to Dr. Merle Umstead of the Fuels Branch for advice and assistance in developing the gas chromatographic procedures.

REFERENCES

1. Platt, V.R., "Chemical Constituents of Submarine Atmospheres," Chapter 1 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R.R., and Platt, V.R., editors, NRL Report 5465, Apr. 21, 1960
2. Saunders, R.A., "The Role of Infrared Spectroscopy in Submarine Habitability," Chapter 5 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R.R., and Platt, V.R., editors, NRL Report 5465, Apr. 21, 1960
3. Johnson, J.E., and Williams, F.W., "Trace Organic Contaminants in the Atmosphere of USS HENRY CLAY," NRL ltr rpt 6180-228A:JEJ:ec, Dec. 8, 1966
4. Johnson, J.E., Saunders, R.A., and Umstead, M.E., "Chlorinated Organic Compounds in Nuclear Submarine Atmospheres; comments on," NRL ltr rpt 6180-150A:JEJ:ec, Jul. 17, 1963
5. Johnson, J.E., "Organic Contaminants - Sources, Sampling, and Analysis," Chapter 2 in "Fourth Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Lockhart, L.B., Jr., and Platt, V.R., editors, NRL Report 6251, Mar. 23, 1965
6. Ravner, H., and Zisman, W.A., "A Survey of Possible Substitutes for Carbon Tetrachloride as Nonflammable Solvents for Shipboard Use," NRL Memo Report 364, Sep. 1954
7. Christian, J.G., and Johnson, J.E., "Catalytic Combustion of Nuclear Submarine Atmospheric Contaminants," NRL Report 6040, Mar. 20, 1964

8. Christian, J.G., and Johnson, J.E., "Catalytic Combustion of Atmospheric Contaminants over Hopcalite," *Inter. J. Air. Water Pollution* 9:1 (1965)
9. Thomas, F.S., "The Elimination of the Oxidizable Contaminants in Submarine Atmospheres by Combustion," Chapter 7 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R.R., and Piatt, V.R., editors, NRL Report 5465, Apr. 21, 1960
10. Johnson, J.E., and Musick, J.K., "Studies of Halogenated Hydrocarbons, Part I - Stability of Fluorocarbons and Chlorofluorocarbons in Contact with Heated Hopcalite Catalyst or Stainless Steel," NRL Report 6546, June 1967
11. Williams, D.D., Johnson, E.T., and Miller, R.R., "A Method for the Determination of Strong-Acid Vapors in the PPM Range," NRL Report 6332, Oct. 14, 1965
12. "Military Specification - Lithium Hydroxide (LiOH), Technical," MIL-L-20213D (Ships), Dec. 11, 1959
13. Gadomski, S.T., "Dry-Packed Beds for the Removal of Strong-Acid Gases from Recycled Atmospheres," NRL Report 6399, Aug. 1966
14. Crummett, W.B. and Stenger, V.A., "Thermal Stability of Methyl Chloroform and Carbon Tetrachloride," *Ind. Eng. Chem.* 48:434 (1956)
15. Stefanescu, P., "Influence of Temperature and of Some Metals on the Stability of Chloroform, Methyl Chloroform and Carbon Tetrachloride," *Revista de Chimie*, No. 9, pp. 524-526 (1959). NRL Translation 1028, prepared by U.S. Joint Publication Research Service, 24 Jun. 1965
16. Barton, D.H.R., and Onyon, P.F., "The Pyrolysis of 1,1,1-Trichloroethane," *J. Am. Chem. Soc.* 72:988 (1950)
17. Molera, M.J. and Ariza, F., "Pyrolysis of Chlorinated Ethylene," *Anales Real. Soc. Espan. Fis. y Quim. (Madrid)* 54B:389-400 (1958); C.A. 53:18848H
18. Bashford, L.A., Emeleus, H.J., and Briscoe, H.V.A., "The Oxidation of Chloroacetylene and Bromoacetylene," *J. Chem. Soc.* 1358 (1938)
19. Sjöberg, B., "Thermal Decomposition of Chlorinated Hydrocarbons," *Svensk. Kem. Tidskr.* 64:63 (1952) (in English)
20. Huntress, E.H., "Organic Chlorine Compounds," New York: Wiley 1948
21. Nicodemus, O., "Pyrogenic Decomposition of Tetrachloroethane and Trichloroethylene," *J. Prakt. Chem.* 83:312 (1911)
22. Erdmann, E., "Autooxidation of Trichloroethylene," *J. Prakt. Chem.* 85:78 (1912)
23. Krynnitsky, J.A., and Carhart, H.W., "Pyrolysis and Chlorinolysis of Some Perchlorinated Unsaturated Compounds," NRL Report C-3468, 20 Jun. 1949; "Pyrolysis and Chlorinolysis of Some Perchlorinated Unsaturated Hydrocarbons," *J. Am. Chem. Soc.* 71:816 (1949)

DOCUMENT CONTROL DATA - R & D		
1. REPORTING ACTIVITY (Complete author.) Naval Research Laboratory Washington, D.C. 20390		2. REPORT SECURITY CLASSIFICATION Unclassified
3. REPORT TITLE HALOGENATED HYDROCARBONS, PART 2 - DECOMPOSITION OF SELECTED CHLORINATED HYDROCARBONS OVER HOPCALITE CATALYST		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) An interim report on a continuing problem.		
5. AUTHOR(S) (First name, middle initial, last name) J. Enoch Johnson Richard H. Gammon		
6. REPORT DATE July 20, 1967	7a. TOTAL NO. OF PAGES 18	7b. NO. OF REFS 23
8a. CONTRACT OR GRANT NO. NRL Problem C08-30	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6582	
b. PROJECT NO. SF-013-08-03-4092	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. 4093		
d. 4094		
e. 4095		
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command) Washington, D.C. 20360
13. ABSTRACT A study was made of the decomposition of several chlorocarbons in air when exposed to Hopcalite catalyst in a laboratory reactor from 50° to 350°C. The chlorocarbons studied were methyl chloroform, vinylidene chloride, trichloroethylene, and tetrachloroethylene. At 300°C the percentage decomposition ranged from 70% for tetrachloroethylene to 100% for methyl chloroform. All yielded substantial amounts of hydrochloric acid as they decomposed. Yields of organic compounds during the decomposition of the chlorocarbons were quite small, except in the case of methyl chloroform, which yielded as much as 50% of vinylidene chloride.		

Security Classification

REF WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hopcalite catalyst						
Methyl chloroform						
Vinylidene chloride						
Trichloroethylene						
Tetrachloroethylene						
Submarine atmospheres						
Chlorocarbons						
CO/H ₂ burner						
Hydrochloric acid						